

HIGH TEMPERATURE APPLICATIONS OF STRUCTURAL CERAMICS

QUARTERLY PROGRESS REPORT

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I. SUMMARY OF PROGRESS TO DATE

Brief Summary

1. High Temperature Fracture of Structural Ceramics

Four-point bend tests on notched bars of Si_5AlON_7 were completed and the results compared with previous work on a yttria-doped silicon nitride (NCX 34) and with literature values for other silicon nitrides. The NCX 34 appears most promising and further tests will be carried out on it and other research grade materials recently received. Reduced scale testing rigs are being made to test small billets of experimental materials.

2. Crack Growth Mechanism Maps

Preliminary maps for Si_3N_4 have been drawn. A computer program for automatically drawing maps from K-v data has been written. Data for SiC has been collected. A new mechanical analysis of 4-point bending has been completed to get K-v data from load-deflection curves.

3. Thermochemical Data

Experiments with heating Si_3N_4 in $95\text{N}_2:5\text{H}_2$ at $\sim 1750^\circ\text{C}$ in various container materials indicated that Mo was a suitable container for short term heat treatments. High temperature x-ray diffraction experiments were initiated with mixed α - β Si_3N_4 specimens.

4. Kinetics of Oxidation

Comparison by x-ray powder diffraction of two billets of Si_3N_4 containing approximately 8 wt % Y_2O_3 failed to show any difference in the phase analysis that could account for the observed difference in low-temperature oxidation resistance. The two billets contained nearly equal amounts of WSi_2 before oxidation, but this compound could not be detected in a specimen that had been severely damaged by oxidation for 20 hours at 735°C . The study was undertaken at the request of Dr. Nancy Tighe as part of her work on NBS-DoE contract EA-77-A-01-6010.

Articles Published and Talks Presented

"A Review of Deformation and Fracture Mechanism Maps with an Introduction to Crack Growth Mechanism Maps," R. J. Fields, Penn State Materials Science and Engineering Seminar, Pennsylvania State University, College Park, Pennsylvania, February 14, 1980.

II DETAILED DESCRIPTION OF TECHNICAL PROGRESS

1. High Temperature Fracture of Structural Ceramics (E. R. Fuller, Jr., R. J. Fields, L. Chuck, and D. Harne)

Progress: Contact was established with two sources of research grade silicon nitrides and sialons. We have received from Dr. K. Kobayashi of the National Industrial Research Institute of Kyushu the following materials: 15 billets of Si-Al-O-N compounds which include billets of single phase $\text{Si}_{6-2}\text{Al}_2\text{O}_2\text{N}_{8-2}$ where z equals 1, 1.3, 2.3, and 3 as well as billets of two phase sialons consisting of 15R-AlN and 12H-AlN polytype phases. He has sent along the complete fabrication procedures for these materials.

We have also received a number of bars of silicon nitride + garnet materials from Prof. Tien of the University of Michigan. These hot-pressed β' - Si_3N_4 bars contain about 10% refractory garnet and varying minute amounts of platinum³chloride nucleating agent. They are in a variety of heat-treated conditions.

Two billets of Kobayashi's sialon ($z=1$) were cut into notched bars (10 x 5 x 50 mm. with a 3 mm. deep notch in the 10 mm. direction) for toughness measurements, and double torsion specimens (25 x 75 x 1 mm.) for crack growth and toughness measurements. The notched bars have been tested in four point bending. These results may be compared with the data which was obtained here for yttria doped silicon nitride (NCX 34) prior to the inception of the present project. Since both materials were tested by the same technique, the results are directly comparable.

To measure a valid K_{IC} , the fracture must initiate from a sharp crack or notch. In both of the above materials, a sharp stable crack was grown from the blunt machined notch by bending the specimen at an elevated temperature (1400 °C for NCX 34 and 1500 °C for the sialon). Since this deformation introduced residual stresses around the crack tip, the specimen was annealed at the pre-cracking temperature for one hour in order to relax these stresses. These pre-cracked bars were then loaded to fracture at various displacement rates and temperatures in air.

A fracture toughness was determined as the critical stress intensity factor at which the specimen fractured catastrophically. This measure of K_{IC} is not in accord with method E399 of ASTM because that procedure does not allow for time dependent effects. Nevertheless, the same critical point that we record here has frequently been used in fracture studies of ceramics, and identified as K_{IC} . The toughness of the sialon and the NCX 34 are plotted as a function of temperature in Fig. 1 together with published data for NC 132, HS 130 (commercial grades of hot-pressed silicon nitride) and HS 350 (a commercial grade of reaction-bonded silicon nitride).

The hot pressed sialon is distinctly less tough than any of the hot pressed silicon nitrides, though it is comparable to or better than, the reaction bonded silicon nitrides. Additionally, we observed evidence of melting on the fracture surface (Fig. 2) and severe oxidation of the specimen's surface at 1500 °C (Fig. 3). The melting may be due to the sialon not being single phase. On fracture surfaces obtained at room temperature we observed light needles and dark spots (Fig. 4). EDAX did not indicate the presence of any heavy metal impurity. We concluded that complete mixing had not occurred in the fabrication process.

This information is being communicated to the source of the material. It is hoped that greater homogeneity will improve this material as further work on this particular lot of Si_5AlON_7 is not justified.

In contrast, the NCX 34 tested in the same manner showed a much higher toughness than all previously tested silicon nitrides. This material also showed a strong effect of strain rate on toughness (Fig. 5), again, in contrast to the sialon which showed no such dependence. The results of the work on NCX 34 have been written up for publication. Further experiments on this material will be carried out as it is the most promising material tested so far.

A three-station, instrumented creep and creep-fracture test facility has been designed and will be constructed when approval is obtained for the equipment expense. A prototype double-torsion fixture has been constructed for use in a universal testing machine equipped with a high-temperature vacuum furnace. The performance of this fixture is being evaluated on a well-characterized glass at moderate temperatures and results indicate that the design is reliable. A similar fixture will be fabricated from tungsten and/or SiC for use at high temperatures in vacuum and in hydrogen-argon or hydrogen-nitrogen gaseous mixtures. A special "cold-tip" has been constructed to reduce the partial pressure of water vapor in these hydrogen gases to the vapor pressure at 77 K.

Plans: More fracture toughness and crack growth measurements will be made on the NCX 34, the silicon nitride - garnet material and on single phase sialon of other compositions. Fracture mechanics specimens will be prepared for two additional commercial grades of silicon nitride: a hot-pressed material (NC 132) and a reaction bonded material (NC 350). A high-temperature, double-torsion fixture will be fabricated for use in the vacuum/reducing environment furnace. Reduced scale, four-point bend rigs are being made to handle specimens made from some of the small billets of research grade materials.

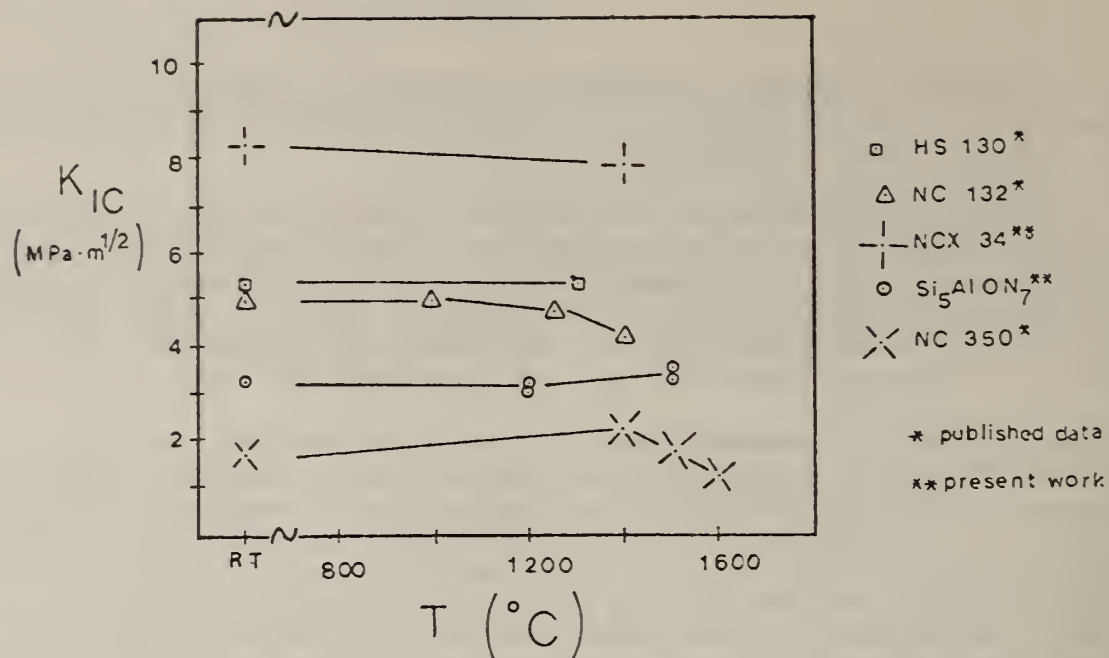


Fig. 1 Critical stress intensity factors for various materials as a function of temperature.



Fig. 2 Crack surface of Si_5AlON_7 showing evidence of melting at 1500°C.

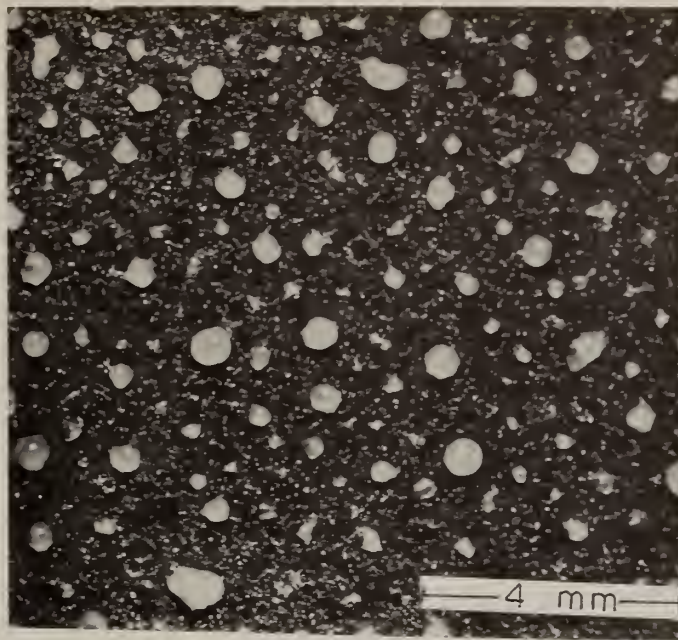


Fig. 3 Originally smooth side surface is severely oxidized after 1 hour at 1500°C.

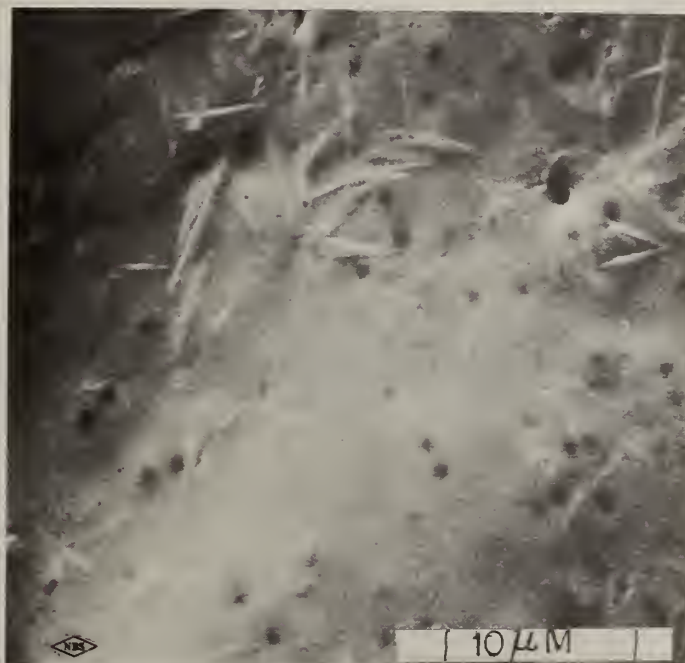


Fig. 4 Room temperature fracture surface exhibits white needles and dark spots.

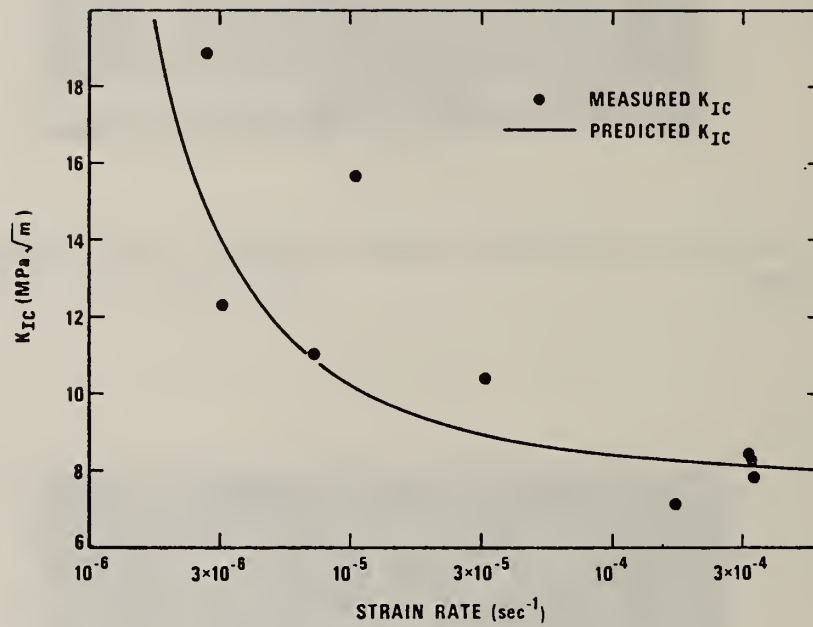


Fig. 5 Critical stress intensity factor for NCX 34 at 1400°C as a function of strain rate.

2. Crack Growth Mechanism Maps (R. J. Fields and E. R. Fuller, Jr.)

Progress: A preliminary crack growth mechanism map (Fig. 6) has been constructed for a commercial, hot-pressed silicon nitride (HS-130). A computer program has been written in BASIC which maps K-v (stress intensity factor versus crack velocity) data with contours of constant temperature onto a map of K-T (stress intensity factor versus temperature) with contours of constant crack velocity. The program uses a theoretically based equation for thermally activated, mechanically assisted crack growth to analyze the data.

Only a small amount of crack growth data for SiC was found in the literature. It was decided to use an analysis of fracture life time as a function of stress to determine the coefficient (A) and exponent (n) for a crack growth law of the form

$$v = AK^n$$

Even so, the data on this material are sparse and either more data will have to be found or actual experiments carried out before a map can be drawn.

An original analysis of four point bending was made in which stress intensity factor-velocity (K-v) data could be obtained without any assumption about the general functional form as required above. This analysis will be used in Task One to provide data for use there and in this task. The analysis is based on knowing the compliance of a notched bend bar as a function of crack length. We have determined this function and can invert it numerically. Hence, we know crack length as a function of compliance. The compliance of a creep resistant material in which a crack is growing is closely approximated by the secant modulus. So at any point on the load deflection curve, we can get crack length and load, and from these two quantities, K. Between successive points on the curve we can get $\Delta a / \Delta t$ (change in crack length per interval of time), i.e. crack velocity, and associate this with the mean K value.

Plans: Establish the validity of the above K-v analysis against known crack lengths in sialon and NCX 34 (yttria doped β' Si_3N_4). If it works, generate K-v curves for these materials at various temperatures.

Complete data collection for SiC and use life-time analysis to get K-v curves for this material. Construct crack growth mechanism map for SiC if possible without further experimental measurements.

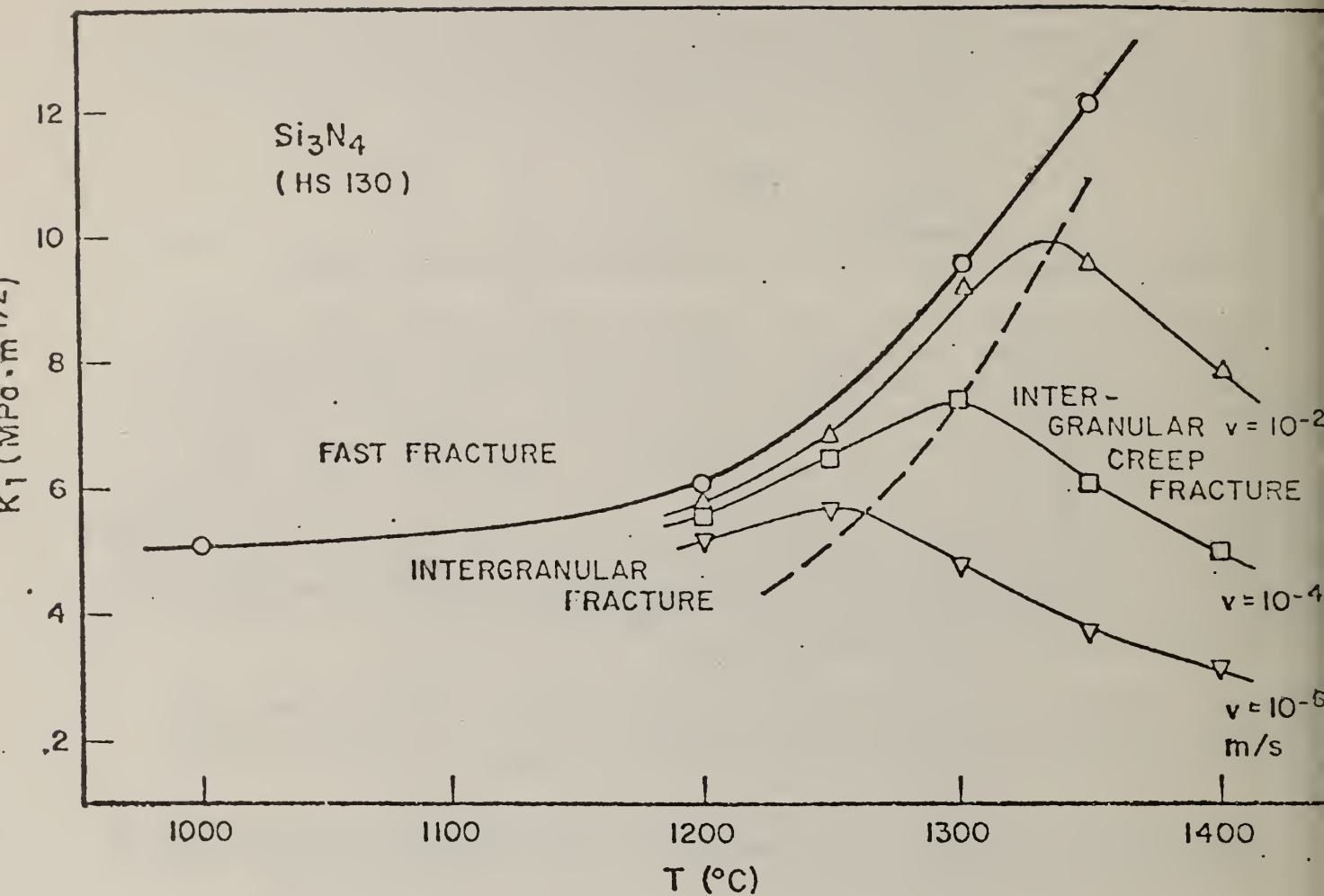


Figure 6. Crack growth mechanism map constructed for silicon nitride.

3. Thermochemical Data (R. S. Roth, J. L. Waring)

Progress: A program was initiated to investigate the thermodynamics of the so-called $\alpha \leftrightarrow \beta$ transition in Si_3N_4 . Candidate materials from five commercial sources of Si_3N_4 were analyzed by x-ray powder diffraction. Various mixtures of the following phases were found to occur: $\alpha\text{Si}_3\text{N}_4$; $\beta\text{Si}_3\text{N}_4$; $\text{Si}_2\text{N}_2\text{O}$; Si and unknown phase(s), depending on the source. Only one small specimen prepared by the CVD process was found to be single-phase $\alpha\text{Si}_3\text{N}_4$ and none contained single-phase $\beta\text{Si}_3\text{N}_4$. From the above it is evident be seen that specimens of single phase material must be obtained in sufficient quantities for use as starting materials for future preparations.

Because single phase Si_3N_4 was not immediately available, some preliminary work was initiated to determine an appropriate container material heat Si_3N_4 . An available sample containing $\beta\text{-Si}_3\text{N}_4 + \alpha\text{-Si}_3\text{N}_4 + \text{Si}$ was heated in three container materials in forming gas (95% $\text{N}_2 + 5\% \text{H}_2$) at about 10^{-16} atm partial pressure of oxygen to the melting point of Pt (1769 °C) by induction heating. The susceptor for these experiments was a covered Mo crucible 1 5/8" long, by 1 3/16" diameter with a .056" sight orifice. In the interior of the outer susceptor crucible was placed a second small test crucible 7/16" long x 1/2" diameter of either Mo, BN, or W containing the 3 phase mixture of Si_3N_4 . The test crucible and the susceptor were isolated by ZrO_2 . The duration of each heating was approximately two hours and temperature was measured with a disappearing filament optical pyrometer.

In the first experiment no reaction was detected between the Mo test crucible and " Si_3N_4 ." In the second experiment a test crucible was fabricated from hot pressed BN obtained from a commercial supplier. This test crucible-plus-" Si_3N_4 " specimen was heated similarly. After cooling, the Si_3N_4 specimen contained glassy-like intrusions and the walls of the BN crucible were severely eroded. The BN from this supplier appears to be unsuited for this work. The material causing the problem may be derived from an impurity within the hot pressed BN.

In the last experiment of the series, a W crucible with " Si_3N_4 " was heated similarly. The surface of the W crucible appeared to be severely etched with grain growth. The x-ray pattern of material taken near the wall of the W test crucible appeared to contain only α and $\beta \text{Si}_3\text{N}_4$ and did not appear to be significantly different from the material heated previously in Mo.

To investigate the effect of W in contact with Si_3N_4 in forming gas, a mixture of 95% Si_3N_4 and 5% W was heated at 1750 °C. The resultant reaction products were examined by x-ray powder diffraction and found to contain a mixture of $\alpha\text{-Si}_3\text{N}_4 + \beta\text{-Si}_3\text{N}_4$ and a small amount of a phase which was identified as WSi_2 . The phase was probably formed by the reaction of the free Si in the starting material with the container W. Although the existence of a similar phase MoSi_2 has been reported in the literature it was not detected in the experiment utilizing a Mo container.

A modified M.R.C. high temperature powder diffractometer has been set up for Si_3N_4 work. This apparatus employs a ribbon element which serves as a heater and specimen holder. From the foregoing discussion, Mo was selected as the most suitable heater material for this work. For the first high temperature x-ray experiment, a heater with a thickness of about .005" was fabricated. A 0.030 g specimen of Si_3N_4 was placed in the cavity of the heater. The specimen was aligned with respect to the diffractometer and the x-ray source. Diffraction intensity was too low, initially, due to both absorption by the beryllium window between the detector and the specimen, and to an insufficient amount of a specimen material composed of low atomic number elements (Si & N). To compensate, a larger than normal amount of specimen was required to obtain adequate x-ray intensity. The x-ray chamber was evacuated and purged several times with forming gas (95% N_2 , 5% H_2). The forming gas was allowed to flow and escape the system through a bubbler. At maximum voltage the power dissipated (100A at 1.6 V) was only 160 watts and the temperature was only 900 °C. To complicate the experiment, the test material temperature did not adhere to the surface of the heater and large temperature gradients were observed on the surface.

In the second experiment, a .001" thick Mo strip was employed as a heater and a maximum temperature of 1320 °C was obtained in forming gas before burnout. The power dissipated was approximately 336 watts.

In the third experiment a .003" heater was employed and full power efficiency was obtained. In addition, the Si_3N_4 was applied by a different procedure in an attempt to produce a thin adherent coat. The Si_3N_4 was very finely ground and suspended in acetone and drops of the suspension were placed on the Mo heater. This procedure yielded a thin, uniform coat with sufficient thickness to produce proper x-ray intensity. This material was heated to temperatures in excess of 1450 °C. At 1486 °C for 5 minutes, the diffraction pattern for the Si_3N_4 disappeared. Room temperature examination showed that all of the material volatilized from the surface of the Mo heater. The platinum rhodium thermocouple welded to the bottom of the heater was attacked by the volatilized material although it was not in contact with the Si_3N_4 .

In the last experiment the specimen mounting procedure was duplicated; the temperature was increased at approximately 100 °C intervals. The same three phase mixture (β - Si_3N_4 , α - Si_3N_4 , +Si) of Si_3N_4 was examined by x-ray diffraction from room temperature to about 1400 °C. The relative amounts of each phase remained approximately the same over the range - nothing disappeared. The reported unit cell for β - Si_3N_4 is hexagonal with $a_0 = 7.603\text{\AA}$, $c_0 = 2.909\text{\AA}$. In this experiment the following diffraction peaks were monitored over the temperature range: (210) (101) for β - Si_3N_4 and (210) (102) for α - Si_3N_4 . At about 700 °C some apparent splitting of the (101) in β - Si_3N_4 was observed, but this may be merely instrumental in nature. More work will be needed to delineate the problem.

Plans: Continue the high temperature investigation of the so-called $\alpha \leftrightarrow \beta$ transition in Si_3N_4 . Assemble, test and calibrate a high-temperature, inert atmosphere furnace for long term equilibrium heating.

4. Kinetics of Oxidation (F. A. Mauer and C. R. Robbins)

Progress: In collaboration with Dr. Nancy Tighe of NBS two billets of hot pressed Si_3N_4 , containing approximately 8 wt% Y_2O_3 as a densification aid, have been examined by x-ray powder diffraction. Dr. Tighe has studied the oxidation resistance and microstructure of these materials by optical methods and TEM as part of her work on NBS-DoE contract EA-77-A-01-6010. One of the billets (labeled NASA billet No. 3) showed conspicuously poor oxidation resistance at low temperature ($\sim 735^\circ\text{C}$) compared to the second, although it was supposed to be identical in composition and processing. The x-ray examination was undertaken at the request of Dr. Tighe to detect differences in the phase composition of the two billets that could account for the difference in low temperature oxidation resistance. It provided an opportunity for us to gain familiarity with the phases encountered in the system Si_3N_4 - SiO_2 - Y_2O_3 and to determine suitable heating schedules for oxidation studies.

Both of the billets examined had a nominal Y_2O_3 content of 8 wt%, but an analysis of billet No. 3 showed that the actual content was 5.5 wt%. In the earlier test of oxidation resistance a bar approximately 100mm long and 6.4mm x 3.2mm in cross section had been cut from billet No. 3 and heated in air for 20 hours with a gradient of $\sim 650^\circ\text{C}$ over the length of the bar. The high temperature end, heated to 1380°C , showed no change, whereas the end heated at 735°C had changed from black to grey, had swollen measurably, and had cracked into several pieces.

The x-ray study (carried out in collaboration with Clyde L. McDaniel of Division 562) consisted of a comparison of the phase composition for four samples: 1) material from the grey (low temperature) end of the bar, 2) material from the black (high temperature end), 3) material from billet No. 3 as received (no oxidation), and 4) material from the second billet, which had shown no evidence of low temperature oxidation. Phase identification is based on comparison with reference patterns for phases in the system Si_3N_4 - SiO_2 - Y_2O_3 and related systems¹⁻⁴.

In all cases, the primary phase was β - Si_3N_4 which constituted 80 to 90% of the sample. There was no detectable α - Si_3N_4 phase. In all cases there were 6 or 8 weak lines that have been tentatively identified as the H-phase of Lange et.al. (1976). Although there does not seem to be general agreement, the composition of this phase as given by Lange is $\text{Y}_{10}\text{Si}_7\text{O}_{23}\text{N}_4$. A more prominent phase, which occurs in nearly equal concentration in samples 2, 3, and 4, but not in sample 1, has been identified as Si_2W . The amount is estimated to be from 3% to 10%. The source of contamination is undoubtedly WC balls used in milling the powder. WC has often been mentioned as an impurity in Si_3N_4 . For example, Lange estimated the WC contamination of his samples to be in the range 1.5 - 3 wt% and reported that "the trace amounts of WC also disappeared during oxidation". No oxides of silica were detected in any of the x-ray patterns (including patterns of the surface of the oxidized bar as well as of pulverized material).

These results fail to show any difference in the phase composition of the "good" and "bad" $\text{Si}_3\text{N}_4(\text{Y}_2\text{O}_3)$ as received. Loss of the Si_2W contaminant was the only conspicuous change accompanying disintegration of the material from billet No. 3 during heating in air at 735 °C. Any oxidation that occurred must have resulted in glassy phases or crystallites too small to produce good x-ray diffraction lines. It is quite possible that many hours of heating are required to crystallize the equilibrium silicate phases.

One question remaining is, what became of the Si_2W ? Did it form a glassy phase on oxidation, or did it form a volatile compound?

Plans:

Samples are being prepared for examination by energy dispersive x-ray spectroscopy in the SEM to compare the tungsten content of material from the grey (low temperature) end of the bar with that from the black (high temperature) end. The results should give important clues as to the role of tungsten in the oxidation of hot-pressed Si_3N_4 . Samples will be oxidized at higher temperatures and for longer times in order to obtain detectable amounts of oxidation products and to promote devitrification so that the phase composition can be determined by x-ray powder diffraction.

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